REMARKS

This Office action is responsive to the Final Rejection mailed January 23, 2004. Support for the amendment of claim 1 is found in original claim 7. Support for the amendment of claim 14 is found in original claim 16. Claims 23 and 24 have been amended by deleting specific structures excluded by amended claims 1 and 14. New claims 27 and 28 have been inserted to provide further limitation to the azinyl boron compound to methene groups having H, alkyl or aryl substituents, as supported at page 5, line 4, of the specification.

Table 1 of the present application contains data that confirms the improved efficiency of dyes having further fused rings on the azinyl rings as in Inv-1 and Inv-4 over dye Inv-5. Dye Inv-5 does not contain a ring fused to one of the azinyl groups as required by amended claim 1 and is relatively inefficient.

The rejection of claims 1-11, 13-23, 25, and 26 under 35 U.S.C. 103(a) as being unpatentable over Shi et al. (US 5,972,247) in view of "new Laser Dyes", Applied Physics (Berlin), volume 3, no. 1, pages 81-88, (1974) is maintained by the Examiner. It is believed that the Examiner intended to recite Shi US 5,935,721 in view of the later references to Shi '721 and the rejection is so interpreted.

According to the Examiner:

> Instant claim 1 requires an organic electroluminescent device comprising a light-emitting layer containing a host and a dopant where the dopant comprises a boron compounds containing a bis(azinyl)methane boron complex group. Shi '721 teaches an organic electroluminescent device comprising an anode, a cathode and an organic electroluminescent element between the electrodes (see abstract). Shi teaches light-emitting layers commonly comprise host material doped with a guest material.... The dopant is usually chosen from highly fluorescent dyes (see col. 1, lines 29-40) per instant claims 1, 8, 9, and 11. In addition, Shi '721 teaches a light-emitting layer (EML) comprising a host material such as 9, 10-di-(2-naphthyl) anthracene (see col. 6, lines 53-62) derivatives doped with fluorescent dye (see col. 47, lines 59-62) per instant claims 1, 8, and 10. Shi '721 fails to teach specific fluorescent dyes comprising a bis(azinyl)methane boron complex group as required by independent instant claim 1.
>
> Applied Physics teaches, in analogous art, a fluorescent dye with strong intensity, which is identical to instant claim 23 compound "Inv-10" (see page 88, compound V 12) per instant claims 4-7, 14-20, and 23. It would have been obvious to one of ordinary skill in

the art at the time of the invention to have formed a light emitting layer comprising either Alq3 or anthracene derivative host material and have selected a dopant according to "Inv-10", because Shi et al. teaches a light emitting layer comprising an Alq3 or anthracene derivative host material doped with a fluorescent dye and Applied Physics teaches "Inv-10" boron fluorescent dye is a known fluorescent dye with strong intensity. Per instant claims 2, 3, 21, and 22, Shi '721 teaches doping a light emitting layer with 1.0% fluorescent dye (see col. 56, lines 22-27). Shi '721 teaches a light-emitting device with a doped light emitting layer provides highly efficient electroluminescence (see col. 1, liens 43-44). Accordingly, per instant claim 13, it would have been obvious to one of ordinary skill in the art at the time of the invention to have expected a greater luminescence with a doped layer than an undoped layer absent evidence otherwise, because Shi '721 teaches the high efficiency of luminescence of a doped layer. Shi '721 teaches the high efficiency of luminescence of a doped layer. Shi '721 further teaches EL elements may be used for the production of a full color EL display panel (see col. 2, lines 66-67) per instant claim 25. The examples of Shi '721 show the EL devices are subjected to electric current to emit light per instant claim 26 (see col. 52 through col. 58, line 46).

Applicants strongly disagree with the Examiner's analysis and application of the Applied Physics article. Firstly, lasing is not an analogous art. One skilled in the art of OLEDs cannot reliably predict the usefulness of dyes in OLEDs from an elucidation of dyes useful for lasing. Electoluminescence and lasing are inherently different phenomena. The key step of electroluminescence is the spontaneous emission of a photon – a process for emission that does not require any incident radiation. The key step of lasing is stimulated emission – a process for emission in which incident radiation is necessary to effect emission. See the following references: [#1 - Thyagarajan, K. et al. Laser Theory and Applications; #2 - Schafer, FP Dye Lasers; -#3- Pavlopoulos, TG, "Scaling of dye lasers with improved laser dyes", Progress in Quantum Electronics, 26(2002) pp193, 202; -#4- Duarte, FJ et al. Dye Laser Principles, pp 192, 291-294], The efficiency of electroluminescence (spontaneous emission) cannot exceed the quantum yield of fluorescence, and, therefore, a weakly fluorescent dye cannot yield an efficient electroluminescent device. On the other hand, in a lasing process, emission is stimulated and, therefore, even a relatively weakly fluorescent dye can result in strong lasing intensity.

In addition to the quantum yield of fluorescence, lasing and electroluminescence are affected by different sets of molecular properties. For instance, lasing intensity is strongly affected by triplet lifetime, intersystem crossing yields, and triplet-triplet absorption of the emitting dye. In electroluminescence case, these dye properties have negligible effect on efficiency. In contrast, electroluminescence efficiency is strongly affected by a concentration quenching phenomenon whereas lasing is not.

As an illustration, a well performing laser dye DCM can be considered, which is a relatively poor performer in electroluminescent devices. According to attached REF #5 [Chen, C. H. and Tang, C. W., "Design and synthesis of red dopants for electroluminescence" (1993)] the concentration quenching effect is relatively strong in the DCM (fluorescent dye)/Alq(host) system and results in loss in electroluminescence efficiency. A specific design of an electroluminescent dopant is required to achieve desired performance..

Lasing dyes are employed in their liquid state as dissolved in a solvent, whereas the emitters of the present invention are employed in their solid state in the absence of any solvent. Since OLED materials are employed in solid state via vapor deposition, one cannot ignore the fact that the emitters used as dopants for OLEDs must have suitable sublimation and satisfactory breakdown temperatures to permit them to be sublimed and vapor deposited without degradation whereas the needs for Lasing where dyes are used in solution have nothing to do with such characteristics.

In summary, strong lasing intensity of a particular dye in a dye laser does not reliably serve as an indication of useful electroluminescence efficiency and vice versa.

It appears that the Examiner equates the term "highly fluorescent" in Shi for OLED devices with the very different term "hi intensity" in the Applied Physics article for Laser properties. In laser technology, the intensity represents the ratio of the photons out divided by photons in for a liquid dye. The term "high intensity" is not the same as the term "highly fluorescent". It relates to the ability to emit light at a particular narrow wavelength range and the intensity may vary with tuning. This is readily distinguished from the measured spectral emission luminance or quantum yield of the solid compound dispersed in an OLED layer

where the fluorescence is not tunable and is measured in terms of the percentage of light emission per pixel area or light emission per applied watt.

The rejection of claims 1-11, 13-15, and 19-26 under 35 U.S.C. 103(a) as being unpatentable over Shi et al. (US 5,972,247) in view of "Fluorescent Tricyclic beta-Azavinamidine-BF$_2$ Complexes", Sathyamoorthi et al., Heteroatom Chemistry, Vol. 4, No. 6, pages 603-608, 1993 is maintained by the Examiner. This rejection is similar to that above but employs an alternate secondary reference. According to the Examiner:

> Heteroatom Chemistry teaches, in analogous art, a fluorescent dye "compound 3" (see page 604, top right) with a maximum peak wavelength of 468 nm, which is identical to instant claims 23 and 24 compound "Inv-5" per instant claims 4-7, 14-20, and 24. It would have been obvious to one of ordinary skill in the art at the time of the invention to have formed a light emitting layer comprising either Alq3 or anthracene derivative host material and have selected a dopant according to "Inv-5", because Shi et al. teaches a light emitting layer comprising an Alq3 or anthracene derivative host material doped with a fluorescent dye and Heteroatom Chemistry teaches "Inv-5" boron fluorescent dye is a known, intense fluorescent dye for fluorescent applications (see page 603, topmost paragraph right column).

Applicants respectfully disagree with the Examiner's conclusions regarding the teachings of the Hereroatom Chemistry article. The referenced paragraph of page 603 indicates that fluorescence was strong in Dye 1 but was <u>not</u> <u>detected</u> in Dyes 2 or 3. Dye 3 corresponds to a dye of the present invention so <u>was not regarded as fluorescent</u>, contrary to the Examiner's assertion. The Examiner refers to a maximum peak wavelength of 468 nm but this refers to an <u>absorption</u> maximum for the dye and not an emission spectrum, which is what the present invention is concerned with. This passage supports the Applicant's position that one cannot predict emission spectra from absorption data. In any event, it is not seen how a statement that the dye corresponding to INV-5 is not fluorescent renders the invention obvious.

The appropriate analysis for an obviousness rejection under 35 U.S.C. 103 is set forth by the U.S. Supreme court in its opinion in *Graham v. John Deere*, 148 USPQ 459, 467, (U.S. Sup Ct. 1966), where it is stated:

> Under Section 103, the scope and content of the prior art are to be determined; differences between the prior art and the claims at issue are to be ascertained; and the level of ordinary skill in the pertinent
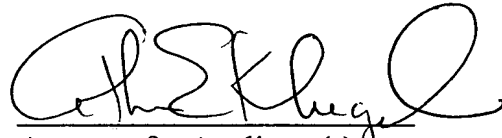
art resolved. Against this background, the obviousness or nonobviousness of the subject matter is determined.

It is settled law that "obvious to try" is not a valid basis for a rejection. *In re Tomlinson et al.*, 363 F2d 928, 150 USPQ 623 (CCPA 1966); *In re Fine*, 5 USPQ 2d 1596 (CAFC 1988). Where the prior art gives no indication of which parameters are critical and no direction as to which of many possible choices is likely to be successful, the fact that the claimed combination falls within the scope of possible combinations taught therein does not render it unpatentably obvious. *In re O'Farrell*, 853 F2d 894, 7 USPQ 1673 (CAFC 1988). In the present application, the examiner has cobbled together non-analogous art in an attempt to infer that it is obvious to use a dye suitable for one purpose for a completely different purpose. There is a clear difference between light absorption and light emission spectra and the these spectra vary as between particular compounds and as between liquids, solids, and solutions of such materials in a solvent..

Newly inserted claims 27 and 28 operate to exclude the structure of dyes of formula V12 of the Applied Physics article from the ambit of the claims. While it is believed that the Applied Physics and Heteroatom Chemistry non-OLED related articles do not render the independent OLED device claims obvious, claims 27 and 28 remove the invention even one further step from the references by limiting the structure scope so as to exclude INV-5 and Inv-10 form the claim coverage.

In view of the foregoing, reconsideration of this patent application is respectfully requested. A prompt and favorable action by the Examiner is earnestly solicited. This amendment should be entered since it places the application in condition for allowance or, in the alternative, in better form for appeal. Should the Examiner believe any remaining issues may be resolved via a telephone interview, the Examiner is encouraged to contact Applicants' representative at the number below to discuss such issues.

Respectfully submitted,

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Enclosures

LASERS

THEORY AND APPLICATIONS

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1

Introduction

An atomic system is characterized by discrete energy states, and usually the atoms exist in the lowest energy state, which is normally referred to as the ground state. An atom in a lower energy state may be excited to a higher energy state through a variety of processes. One of the important processes of excitation is through collisions with other particles. The excitation can also occur through the absorption of electromagnetic radiation of proper frequencies; such a process is known as stimulated absorption or simply as absorption. On the other hand, when the atom is in the excited state, it can make a transition to a lower energy state through the emission of electromagnetic radiation; however, in contrast to the absorption process, the emission process can occur in two different ways.

(i) The first is referred to as spontaneous emission in which an atom in the excited state emits radiation even in the absence of any incident radiation. It is thus not stimulated by any incident signal but occurs spontaneously. Further, the rate of spontaneous emissions is proportional to the number of atoms in the excited state [see Eq. (3.2-3)].

(ii) The second is referred to as stimulated emission, in which an incident signal of appropriate frequency triggers an atom in an excited state to emit radiation. The rate of stimulated emission (or absorption) depends both on the intensity of the external field and also on the number of atoms in the upper state. The net stimulated transition (stimulated absorption and stimulated emission) depends on the difference in the number of atoms in the excited and the lower states, unlike the case of spontaneous emission, which depends only on the population of the excited state.

The fact that there should be two kinds of emissions—namely, spontaneous and stimulated—was first predicted by Einstein in 1917. The consideration which led to this prediction was the description of thermodynamic equilibrium between atoms and the radiation field. Einstein

1

(1917) showed that both spontaneous and stimulated emissions are necessary to obtain Planck's radiation law; this is discussed in Section 3.2. The quantum mechanical theory of spontaneous and stimulated emission is discussed in Section 8.5.

The phenomenon of stimulated emission was first used by Townes in 1954 in the construction of a microwave amplifier device called the maser†, which is an acronym for microwave amplification by stimulated emission of radiation. At about the same time a similar device was also proposed by Prochorov and Basov. The maser principle was later extended to the optical frequencies by Schawlow and Townes in 1958, which led to the device now known as the laser. In fact "laser" is an acronym for light amplification by stimulated emission of radiation. The first successful operation of a laser device was demonstrated by Maiman in 1960 using ruby crystal (see Section 9.3). Within a few months of operation of the device, Javan and his associates constructed the first gas laser, namely, the He–Ne laser (see Section 9.4). Since then, laser action has been obtained in a large variety of materials including liquids, ionized gases, dyes, semiconductors etc. (see Chapter 9).

The three main components of any laser device are the active medium, the pumping source, and the optical resonator. The active medium consists of a collection of atoms, molecules, or ions (in solid, liquid, or gaseous form), which acts as an amplifier for light waves. For amplification, the medium has to be kept in a state of population inversion, i.e., in a state in which the number of atoms in the upper energy level is greater than the number of atoms in the lower energy level. The pumping mechanism provides for obtaining such a state of population inversion between a pair of energy levels of the atomic system. When the active medium is placed inside an optical resonator, the system acts as an oscillator.

After developing the necessary quantum mechanics in Chapter 2, in Chapter 3 we give the original argument of Einstein regarding the presence of both spontaneous and stimulated emissions and obtain expressions for the rate of absorption and emission using a semiclassical theory. We also consider the interaction of an atom with electromagnetic radiation over a band of frequencies and obtain the gain (or loss) coefficient as the beam propagates through the active medium.

Under normal circumstances, there is always a larger number of atoms in the lower energy state as compared to the excited energy state and an electromagnetic wave passing through such a collection of atoms

† A nice account of the maser device is given in the Nobel lecture of Townes, which is reproduced in Part III of this book.

REF # 2

Dye Lasers

Edited by F. P. Schäfer

With Contributions by

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Second Revised Edition

With 114 Figures

Springer-Verlag Berlin Heidelberg New York 1977

4. Structure and Properties of Laser Dyes

K. H. Drexhage

With 6 Figures

An essential constituent of any laser is the amplifying medium which, in the context of this book, is a solution of an organic dye. Since the beginning, the development of the dye laser has been closely tied in with the discovery of new and better laser dyes. The phthalocyanine solution employed for the original dye laser (Sorokin and Lankard, 1966) is hardly used today, but the compound rhodamine 6G, found soon afterwards (Sorokin et al., 1967), is probably the most widely employed laser dye at the present time. In the years following the discovery of the dye laser various other compounds were reported for this purpose. Almost all were found by screening commercially available chemicals, but this source of new laser dyes soon became exhausted. It was reported in 1969 that a survey of approximately one thousand commercial dyes showed only four to be useful (Gregg and Thomas, 1969), and three of these belonged to classes of laser dyes that were already well known. Considering the large number of available chemicals, it is perhaps surprising that so few good laser dyes have been found so far. The reason for this is that some very special requirements must be met by such dyes and this excludes the majority of organic compounds. This chapter is intended to give the reader some insight into the relations between molecular structure and the lasing properties of organic dyes, relations which have recently been applied in the planned synthesis of new laser dyes. In addition, the physicochemical properties of the most important laser dyes are discussed here in some detail.

4.1. Physical Properties of Laser Dyes

Organic dyes are characterized by a strong absorption band in the visible region of the electromagnetic spectrum. Such a property is found only in organic compounds which contain an extended system of conjugated bonds, i.e., alternating single and double bonds. Whereas the light absorption of dyes cannot be derived *rigorously* from their molecular structure owing to the complexity of the quantum-mechanical problem, more or less simple models have been found that are capable of

Fig. 4

Review

Scaling of dye lasers with improved laser dyes

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Abstract

Dye lasers are widely used in spectroscopic research because they provide tunable, coherent radiation. They employ highly fluorescent organic compounds, possessing some specific spectroscopic properties, dissolved in organic solvents. These liquid media are cooled by circulation. The liquid media, the dye solutions, have no scaling limitation. However, large dye lasers that generate high-energy and high average-power outputs do not exist because of the lack of a scalable pump source. Presently, pulsed and CW lasers and short-pulse small flashlamp are mainly used for pumping laser dyes. Only these pump sources are able to overcome the excessive triplet-state losses (TSLs) present in presently available laser dyes. These TSLs result, in part, from fairly large triplet absorption coefficients, $\varepsilon_T(\lambda_F)$, of transient triplet-state dye molecules generated during excitation. Using new laser dyes that possess smaller triplet absorption coefficients should not only improve laser-action efficiencies, but should also allow pumping with large, long-pulse flashlamps and possibly with laser diode arrays and incoherent light sources. These pump sources are scalable and therefore would further increase overall outputs. This paper details TSL, vibronic spin–orbit interactions in heterocyclics, and other spectroscopic parameters affecting laser-action properties. Pump sources for dye lasers, especially flashlamps, are also reviewed. Criteria that can be used to identify candidate laser dyes for efficient long-pulse operation are provided. These are the so-called *quasi*-aromatics (QAs), five- and six-membered heterocyclics, and are identified as possessing small $\varepsilon_T(\lambda_F)$ values. The pyrromethene–BF$_2$ complexes are representatives of such QAs. There should be many candidates that exhibit efficient laser action in different spectral regions, under long-pulse, large flashlamp pumping.

Contents

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region. Some T–T bands are very strong. For example. anthracene (Fig. 1C) has $\varepsilon_T(430) = 9.2 \times 10^4$ l/mol cm.

Reviewing experimental data on T–T absorption of organic compounds, including laser dyes reported in the literature [12–14]. one observes the following. Generally, at least one strong T–T absorption band is present on the long wavelength side of the lowest energy S–S absorption band, covering the FSR and beyond. Often, one or more weaker T–T absorption bands are also present in this spectral region.

The intensity of the strong T–T absorption band. $\varepsilon_T(max)$ often ranges from 1 to 10×10^4 l/mol cm. This is comparable to the intensity with the extinction coefficient $\varepsilon_S(max)$ of the lowest-energy S–S absorption band of organic dyes. All dyes have strong lowest-energy absorption bands, because strong absorption in the visible spectral region generates the impression of color.

Case C in Fig. 3 has the lowest T–T absorption over the FSR of the three cases. Only in this case, one can expect to observe laser action. Indeed, from T–T absorption measurements on laser dyes, case C is present in most commercially available laser dyes. Experimentally, one generally observes $\varepsilon_S(max)/\varepsilon_T(\lambda_F) = 10-15$ [13–15]. Because in (laser) dyes $\varepsilon_S(max)$ is very large, and $\varepsilon_T(\lambda_F)$ of $\frac{1}{10}-\frac{1}{15}$ of $\varepsilon_S(max)$ implies that there is still considerable T–T absorption present in the
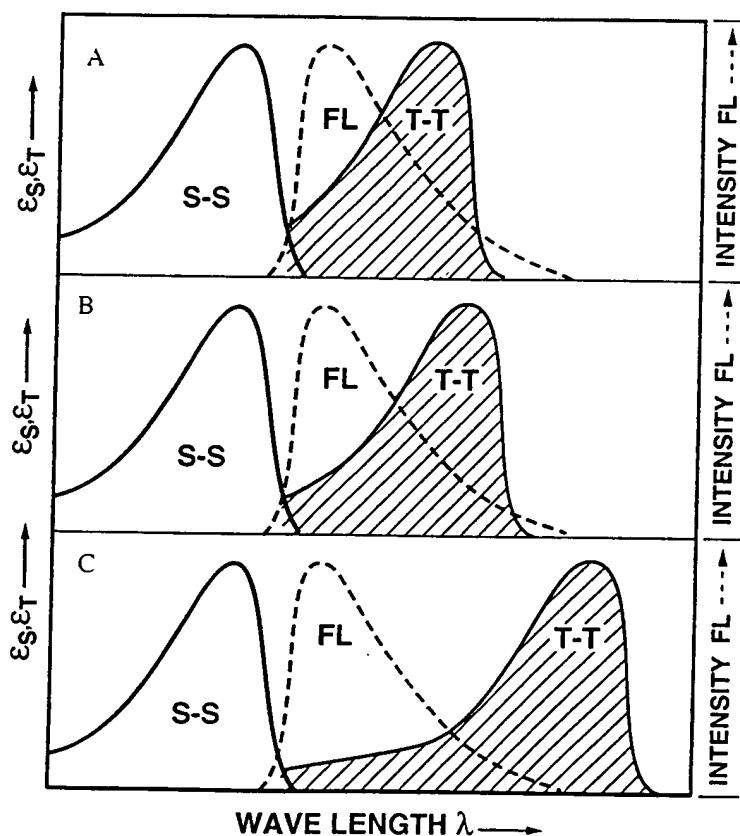

Fig. 3. Depicts three representative cases (A, B, and C) of an organic compound that exhibits strong S–S absorption. Also present is a strong fluorescence. FL, and only one strong T–T absorption band in the FSR.

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DYE LASER PRINCIPLES

With Applications

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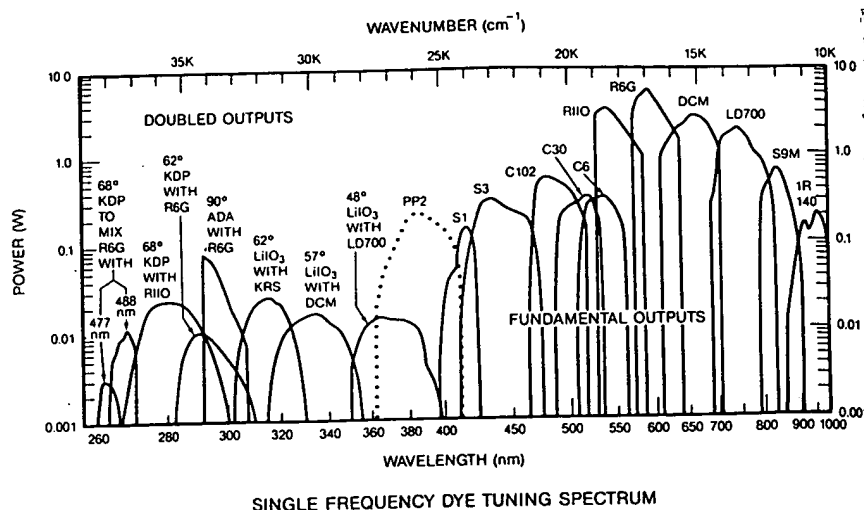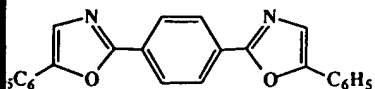
SINGLE FREQUENCY DYE TUNING SPECTRUM

Fig. 5.3 Tuning curves of single-frequency dye-laser radiation, including frequency-doubled and sum frequency mixed outputs. The vertical axis is single-frequency power output displayed as a function of wavelength. The direct dye-laser output spans the spectral region from the blue end of the dye PP2 at $\approx$365 nm to the red end of the dye IR 140 at $=1$ μm. The outputs from the intracavity frequency doubled radiation extends from $\approx$395 to 270 nm. The two curves at the extreme blue and end show the single-frequency power obtained by intracavity sum-frequency-mixing the R6G dye laser radiation with argon-ion laser lines at 488 and 477 nm. These curves are taken with permission from Johnston, T. F. (1987) and have been modified slightly to include the results from Johnston, T. (1988) for the dye PP2 (polyphenl 2).

not a problem for most applications because spectroscopic studies usually have spectral windows that are easily covered by one dye. In fact, with the high resolution (approximately one MHz) of a single-frequency dye laser, there is often more spectroscopic resolution than is needed. Most of the UV outputs indicated in this figure (260–400 nm) are generated by using the strong visible dye-laser outputs and nonlinear optical-mixing methods.

2.3. Dye Characteristics

2.3.1. Absorption and Emission Spectra

The basic design of the cw dye laser is naturally constrained in fundamental ways by the photophysics and chemistry of the dye molecules. In Fig. 5.4 we see the representative absorption and emission spectra of a common laser dye. One of the important things to notice here is that the emission band is lower in frequency (red shifted) and is nearly the mirror image of the absorption band. In addition both the absorption and emission spectra are broadband features without sharp lines, indicative of a multitude of broadened mechanisms and overlapping energy levels. This is

include new structures for specified lasing frequencies, the appearance of water-soluble dyes, the linkage of dyes that provides novel means for energy transfer (down-shifting of output wavelengths), and dyes incorporated in the microstructures of detergent micelles, cyclodextrins, or other binding agents.

2. DYE PHOTOPHYSICS

2.1. Fundamental Photophysical Properties

Laser dyes typically show large absorptivities, as measured by their molar extinction coefficients, ϵ (units of liter/mole cm^{-1} or M^{-1} cm^{-1}). This feature is responsible for the high optical densities associated with moderate concentrations (10^{-4}–10^{-5} M) of dye and results from the high degree of delocalization and polarizability of π electrons in dye structures. The degree to which electron density in a dye molecule is "rearranged" or polarized as the result of absorption of photons is related to the transition dipole moment or oscillator strength (f) for the electronic transition. The parameter f is related to a first approximation, using classical theory (Turro, 1978), to the extinction coefficient (ϵ)

$$f = 4.3 \times 10^{-9} \int \epsilon \, d\nu = 4.3 \times 10^{-9} \, \epsilon_{max} \Delta\nu_{1/2} \qquad (7.1)$$

where ϵ is the experimental extinction coefficient and ν is the energy (in wavenumbers) of the absorption in question. The integral of ϵ is more conveniently approximated by the product of extinction coefficient at the absorption maximum and the width of the absorption band at $1/2\epsilon_{max}$ (Eq. 7.1). The importance of oscillator strength is underscored on noting the relationship between f and the rate constant for radiative decay of an excited dye molecule (here k_f, the rate constant for fluorescence emission),

$$k_f = \nu(max)^2 f \qquad (7.2)$$

where $\nu(max)$ is the energy corresponding to the maximum wavelength of absorption. The probabilities of both spontaneous emission (as reflected in k_f) and stimulated emission (the latter responsible for "gain" or light amplification in a dye-laser cavity) are related to the size of the transition moment and the oscillator strength in the same way.

The most important electronic energy levels for organic dyes in fluid media are the ground state (S_0) and the first electronic excited state (S_1) as shown in Fig. 7.1. The absorption of light which raises molecules to the upper level is associated with promotion of an electron in a bonding orbital
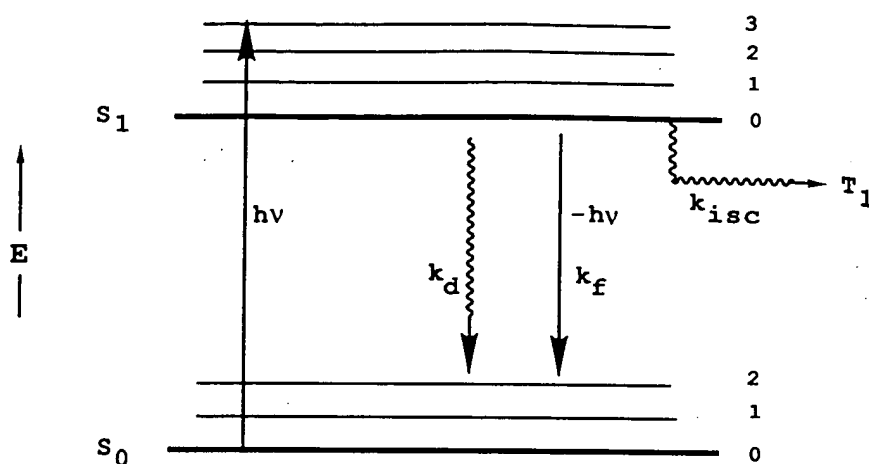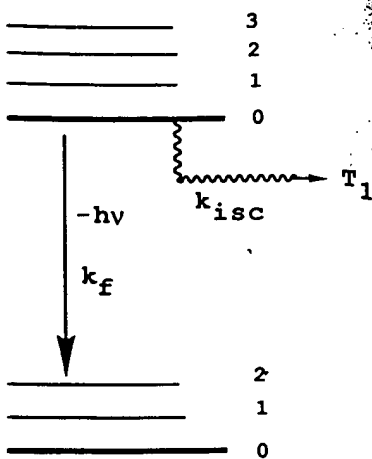
Fig. 7.1 Jablonski state energy diagram depicting molecular ground state (S_0), first excited singlet state (S_1), and lowest triplet state (T_1). Heavy arrows identify radiative (absorption and emission) processes, whereas curly arrows show radiationless transitions. Fluorescence, intersystem crossing, and nonradiative internal conversion occur with rate constants, k_f, k_{isc}, and k_d, respectively. Vibrational energy levels for ground and excited states are numbered.

to an antibonding (virtual) orbital of the molecule. This electronic rearrangement is accompanied by a displacement of the equilibrium nuclear coordinates of the molecule; the vibrational energy states associated with these nuclear coordinate changes are depicted by the subspacings of Fig. 7.1. Thus, the dye laser may be viewed as a "four-level" system in that the most probable excitations proceed to populate upper vibrational levels in S_1, a vibrational relaxation to the "zeroth" level in S_1 follows, and emission occurs to repopulate an upper vibrational level of the ground state (S_0).

Sauers *et al.* (1987) and Piechowski and Bird (1984) have noted that the most common laser dyes are not optimally designed for laser action with respect to the shaping of the absorption–emission bands of organic dyes which are broadened due to vibrational (rotational) relaxation. They reason that absorption and emission strength is associated with 0–0 transitions for which the probability of stimulated emission (to the overpopulated lowest ground state) is low. The absorption and emission spectra for the well-known xanthene dye, rhodamine B, are shown in Fig. 7.2 with reference to the position of the peak lasing wavelength. The Rutgers group further proposes that the "shaping" of spectral bands in favor of the "satellites" corresponding to 0–1 or 0–2 transitions can be predicted for synthetically attainable structures. The approach was illustrated with the

.ing molecular ground state (S_0), first
(T_1). Heavy arrows identify radiative
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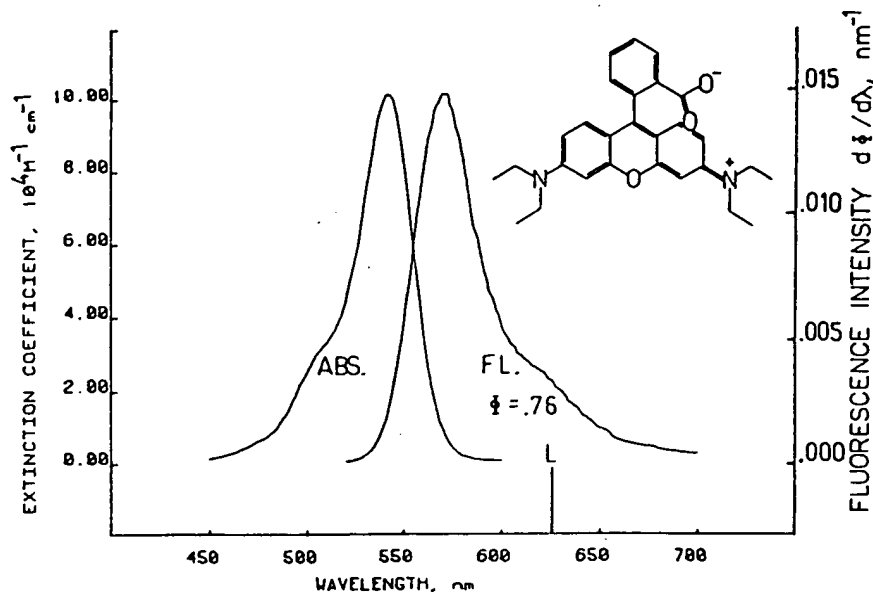:rgy levels for ground and excited states

Fig. 7.2 Absorption and fluorescence spectra of rhodamine B in ethanol. Laser-dye spectra often show this mirror-image relationship. Note also that the peak lasing wavelength (L) is offset from the most intense band for spontaneous fluorescence [reprinted from Sauers *et al.*, 1987].

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transitions can be predicted for
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xanthenone ("rhodamone") dye VII, for which a slightly higher lasing output in the satellite region (559 nm) was observed (Sauers *et al.*, 1987).

The process of dye fluorescence (k_f) must compete with nonradiative decay of excited species by internal conversion to the ground state (k_d). For organic dye molecules, the interaction of electron spin and orbital motion is developed to such a degree that spin-prohibited processes are probable, involving transitions to other excited states (principally, the lowest triplet state). The formation of dye triplets through the process known as intersystem crossing is an interesting but often disturbing artifact of dye photochemistry. The problem has to do with the time evolution of excited species within a laser cavity. The S_1 state responsible for stimulated emission normally displays a lifetime of 1–5 nsec. Due to a spin prohibition for return to the ground state, the lifetime of the triplet (T_1) state can be much longer, typically 10–100 μsec in the absence of any quenching agent. The long lifetime of dye triplets not only ensures buildup of a species that may be chemically reactive (*vide infra*) but also provides a competitive absorber of light at lasing wavelengths.

The important competition among dye fluorescence (k_f), intersystem crossing (k_{isc}), and internal conversion (k_d) is reflected in quantum yields (Φ). For the emission process, the quantum efficiency is the fraction associated with the microscopic rate constants as follows

$$\Phi_f = k_f/(k_f + k_{isc} + k_d). \qquad (7.3)$$

If a photochemical reaction proceeds from the same S_1 state for which preceding processes compete, a similar quantum yield expression involving a reaction rate constant, k_r, is derived:

$$\Phi_r = k_r/(k_f + k_{isc} + k_d + k_r). \qquad (7.4)$$

Laser dyes almost by definition display low quantum yields for intersystem crossing (e.g., triplet yields, $\Phi_{isc} < 0.05$) due to the requirement for high efficiencies for spontaneous fluorescence. Typically, measured fluorescence yields, Φ_f, range from about 0.6 to near the optimum 1.0. However, most organic dyes which do have a nonnegligible triplet yield provide problems, since most triplet absorption (allowed transitions to higher triplet levels) is broad and overlaps the fluorescence (lasing) region (Section 2.3.2).

2.2. Solvent Effects on Dye-Emission Parameters: "Solvent Tuning" of Lasing Wavelengths and Emission Yields

For some time it has been known that the solvent may play a decisive role in laser-dye photophysics (Drexhage, 1973). An instructive example regarding solvent influences involves the series of coumarin dyes studied by Jones et al. (1980a,b,1985a). Substitution of coumarin with an amino group at the 7-position generates a merocyanine chromophore characterized by the conjugation of "push-pull" substituents (amine electron donor and carbonyl (C=O) electron acceptor groups). The pattern of substitution gives rise to an intramolecular charge-transfer (ICT) transition for which there is a large oscillator strength for absorption (S_0–S_1) and a high rate of fluorescence emission. Solvent influences for the coumarins can be understood in terms of the structures VIII (the common structure for coumarin 1) and IX which represent resonance contributors describing, in an approximate way, the electronic states of a typical molecule. A coumarin structure such as VIII is a faithful description of the ground state, whereas IX better represents the altered electron density pattern for the S_1 ICT state. Notably, a much higher dipole moment is predicted for S_1. Substitution of the dye chromophore with additional groups can either elevate or depress the excited-state dipole moment.

The role that solvent plays in stabilizing coumarin dipoles is illustrated in

REF#5

Bibliographic Information

Abstract

The performance of the red org. EL emitter can be optimized by selecting the proper dopants (DCJ vs. DCM) and by
designing and synthesizing dopant mols. with steric bulkiness (DCJT va. DCJ). The steric spacer is important in reducing the
effect of concn. quenching inherent in this class of mols. with strong dipoles. The discrepancy between the PL and EL
dependence on dopant concn. suggests that electron trapping by the more easily reduced dopant plays an important role in
electroluminescence.

CTB

DESIGN AND SYNTHESIS OF RED DOPANTS FOR ELECTROLUMINESCENCE

C. H. Chen and C. W. Tang

1. INTRODUCTION

Recently there is considerable interest in organic materials for electroluminescent (EL) display applications (1-3). For full color displays, it is necessary to show that primary RGB EL emitters with proper chromaticity and sufficient luminance efficiency can be obtained. In principle, the guest-host doped system offers a ready avenue for achieving such an objective, mainly because a single host with optimized transport and luminescent properties may be used together with various guest dopants leading to EL of desirable hue.

We previously reported (1) a doped EL system based on the principle of guest-host energy transfer to effect the spectral shift from AlQ3 to the dopant molecules (Fig. 1). AlQ3 is a suitable host for red EL emitters since its emission at 530 nm is adequate to
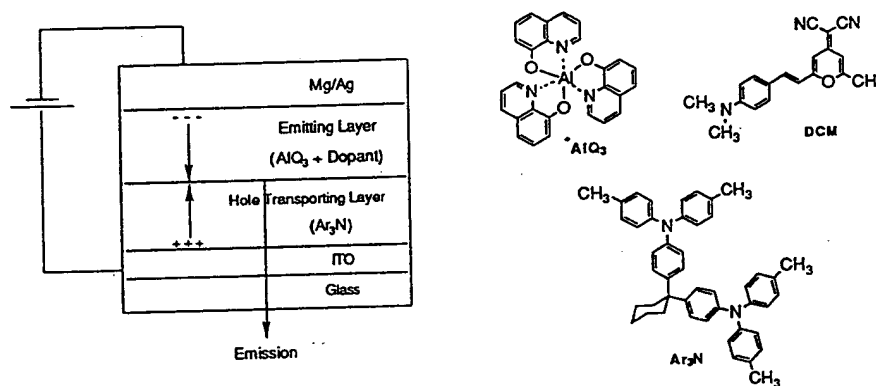

Fig. 1. Organic Guest-Host Electroluminescent Cell.

sensitize guest EL emission in the red spectral region. The dopants chosen to provide the red emission were from the class belonging to DCM. These molecules generally have a high photoluminescence (PL) quantum yield (> 50% in dilute solution) and the position of the emission maxima can be readily shifted by certain modification of the DCM structure. Furthermore, in both PL and EL, a significant red-shift in emissions was observed with increasing dopant concentration in the AlQ3 host. Thus, efficient red EL emitters with

suitable hue can be found among molecules in this DCM class. However, the luminance efficiency of the AlQ3/DCM system is compromised by two factors. First, the spectral bandwidth of the emission is rather broad (FWHM ~100 nm). As a result, a suitable red hue can be obtained only with the dominant emission in the deep red region. The broadness of the emission band yields a significant portion of photons in the long wavelength spectral region when the eye is not sensitive resulting in a loss of luminance efficiency. Second, the EL efficiency of the guest-host system is highly dependant on the concentration of the guest in the host matrix. The concentration quenching effect, presemably due to the aggregation of guest molecules, is relatively strong in the AlQ3/DCM system. A further loss in luminance efficiency would result if a concentrated guest-host system is necessary to provide for an adequate red hue in the EL emission.

Fig. 2. Design Features of Red Fluorescent Dopants.

2. DESIGN AND SYNTHESIS

Aiming to improve the red emission of this organic EL system, we have synthesized and studied the luminescence of a number of new red dopants based on the elaboration of DCM structure. The design features of these fluorescent dyes are schematically shown in Fig. 2 – namely, *chromophoric extension, structural rigidization and steric spacing*. Representative examples of these fluorescent dyes are depicted in Fig. 3.

Fig. 3. Red Fluorescent Dyes Synthesized.

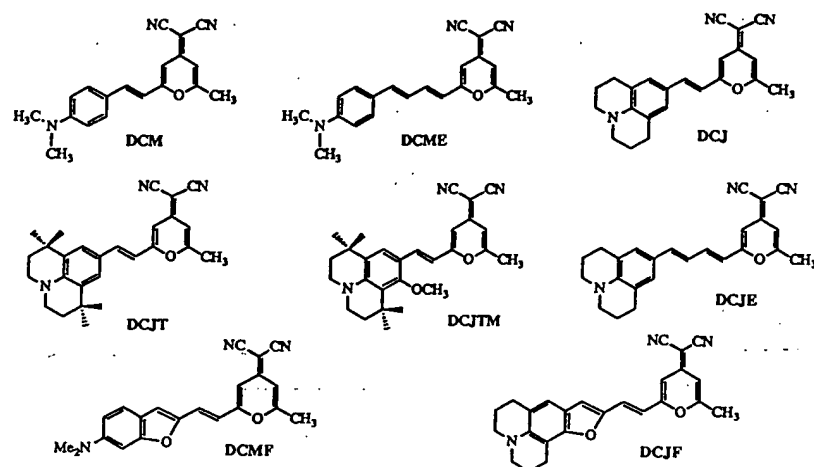Synthesis of dyes with the *tetramethyl* steric spacer incorporated in the *julolidyl* structure was made possible by the availability of the key intermediate, *8-hydroxy-1,1,6,6-tetramethyljulolidine.* (4) which was prepared from *m*-aminophenol in good yield.

The *furan*-fused DCMF and DCJF (5) are not desirable candidates because their PL are shifted too far to the red (near 700 and 755 nm, respectfully), and their emission bands are too broad to be useful. Similarly, the extended DCME and DCJE have a low *luminance* efficiency because of their emission in the deep red spectral region where human eyes are not very sensitive.

Table I. Comparison of Luminescent Properties of DCMs and DCJs.

Dyes	Radiance[a]	Luminance[a]	λ_{max}[b]
DCM	1.00	1.00	596 nm
DCME	0.80	0.22	672 nm
DCJ	1.28	0.62	636 nm
DCJE	1.13	0.11	720 nm
DCJTM	0.51	0.25	636 nm
DCJT	1.86	0.95	632 nm

[a]. Relative to DCM.
[b]. Measured in 1,2-dichloroethane.

Table 1 compares their relative radiance and luminance efficiencies, and emission maxima with those of DCM. It is clear from the Table that DCJ type of structural modification offers the best compromise to shift the DCM fluorescence about 40 nm to the red without suffering concomitant loss of PL efficiency and the undesirable broadening effect of the emission band.

3. RESULTS AND DISCUSSION

Photoluminescence. The effect of concentration quenching of both PL and EL emission can presumably be minimized by reducing the interaction between the guest molucules in the AlQ3 matrix. For the DCM class of molecules where the excited state dipole moment is large due to the strong donor (amine moiety) and accepter (dicyanomethylene) in the chromophore, the excimer emission is likely to occur. Such emission is red-shifted with respect to monomer emission and generally less efficient. We studied the PL of DCJ (Fig. 4) vs DCJTM (Fig. 5) to illustrate the importance of steric group in minimizing the effect of concentration quenching. To maximize the energy transfer between the guest-host system, this onset of concentration quenching should be shifted to as high a guest concentration as possible, resulting in predominantly guest emission without a loss of its emission efficiency. In the case of DCJ (Fig. 4), the minimum concentration of DCJ in AlQ3 required to completely transfer the green AlQ3 fuorescence to the red DCJ fluorescence is about 2.2×10^{-2} M. At this concentration, the concentration quenching of the DCJ emission already begins to set in (by about 15% relative to the maximum radiance obtainable from the DCJ/AlQ3 binary system) resulting in a less efficient system. Further increase in DCJ concentration rapidly causes steeper loss in the overall radiant efficiency, as the emission maximum shifts further to the red. While this red shift is desirable with respect to hue saturation, the loss in radiant efficiency is not tolerable. On the contrary, the DCJTM emission (Fig. 5) in AlQ3 is more immune to the concentration effect due to the *tetramethyl steric spacer*. At the same concentration in AlQ3 (2.2×10^{-2} M). DCJTM has effected a complete fluorescence transfer from the AlQ3 host, resulting in red emission only from DCJTM. More importantly, the high radiance efficiency from DCJTM is maintained even at this concentration. Further increase in DCJTM concentration eventually causes the fluorescence quenching mechanism to set in, but this appears to be at a higher level than DCJ in AlQ3, and the overall sensitivity is smaller in DCJTM even at high concentration. This result suggests that the incorperation of the steric bulky groups onto the DCJ type of dopants tends to suppress the formation of excimers or highter order excited oligomers in a concentrated guest-host system through "spacing" between neighboring guest molecules via steric hinderance.

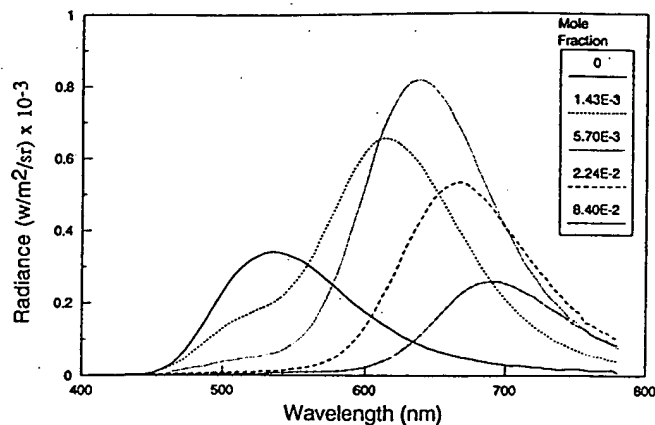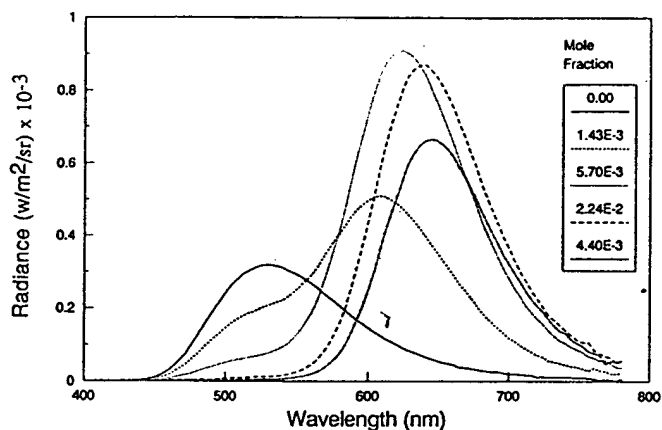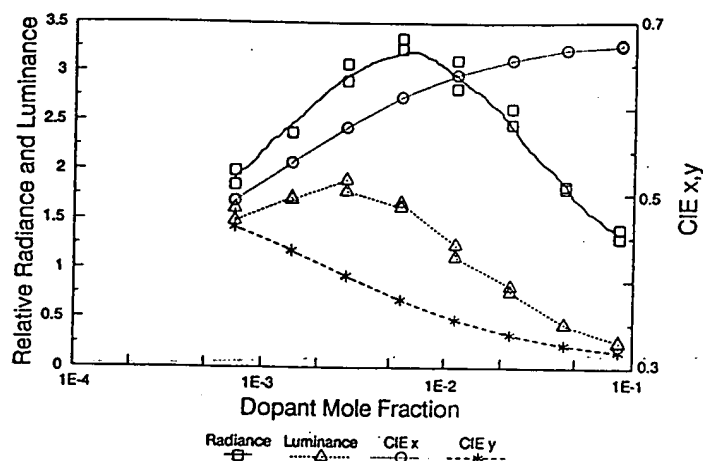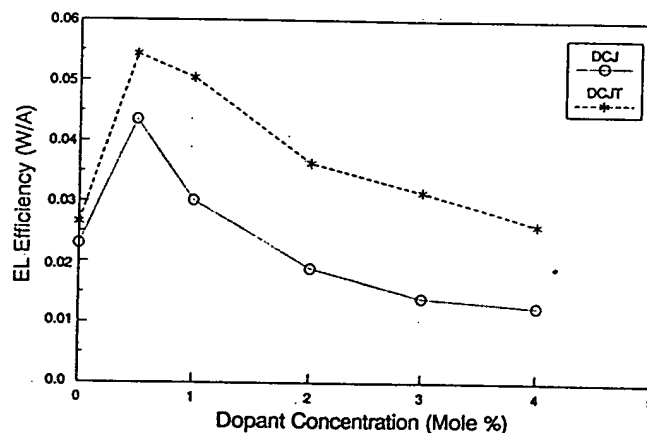Similar results were also obtained from the PL of DCJT/AlQ3 doping experiments. In

Fig. 4. Spectral Radiance vs Dopant Concentration: DCJ/AlQ3.

Fig. 5. Spectral Radiance vs Dopant Concentration: DCJTM/AlQ3.

Fig. 6, the relative luminance of DCJT along with the corresponding $CIE_{x,y}$ coordinates is plotted against its mole fraction in AlQ3. At the desirable red region corresponding to about 1% molar concentration, the DCJT/AlQ3 luminance is about the same as that of the host AlQ3 without dopant, and the CIE coordinates are: x = 0.64; y = 0.36.

Electroluminescence. The concentration dependence of EL efficiency, in principle, ought to resemble that of the PL efficiency, assuming the same emitting species in both cases. In fact, the EL process of the doped system can be rather complicated depending on the nature of the dopant and its interaction with the host, as well as with the adjacent hole transporting layer. Fig. 7 compares the EL concentration dependence of DCJT and DCJ in

Fig. 6. Concentration Dependence of PL: DCJT/AlQ3.

Fig. 7. EL Efficiency vs Dopant Concentration of DCJ and DCJT in AlQ3.

AlQ3 host. Here we found that, for both dopants, the EL efficiency drops off more rapidly with concentration in comparison with their PL. The effect of the steric group in DCJT in offsetting the concentration quenching effect, prominant in the PL process, is also apparent in the EL. For both dopants, the maximum EL efficiency occurs at a dopant concentration of about 0.5%. Analogous to the PL data, the DCJT EL emission falls off less rapidly compared with that of DCJ. The EL efficiency of DCJT only begins to drop significantly when the DCJT concentration is greater than 1%, and it is maintained at an efficiency equivalent to the undoped AlQ3 cell at a concentration as high as 4%. In contrast, the DCJ EL efficiency decreases significantly at 1% concentration, and is about half that of the

undoped cell when the dopant concentration reaches 3 to 4%. Common to both dopants, the absolute magnitude of the EL gain (over undoped AlQ_3) is less than the PL gain at all concentrations. These observations suggest that the origin of the PL and EL luminances may be rather different.
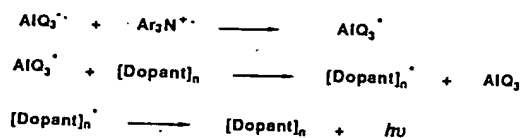
In PL, the excitation penetration is assumed to be relatively uniform throughout the bulk of the doped AlQ_3 film (the excitation wavelength was 405 nm and absorption coefficient of AlQ_3 film is 5×10^4 cm^{-1}). Furthermore, photo excitation yields directly the excited state of AlQ_3 without involving any free charges. In contrast, the EL process is much less spacially homogeneous. In the two-layer structure studied by Tang and VanSlyke (1), the recombination region is presumed to occur at the interface between the hole transport layer and the emitter layer. With undoped AlQ_3 or AlQ_3 doped with molecules which do not affect the charge carrier transport processes, the confinement of the injected charge carriers conceivably occurs at the interface because of the existence of potential barriers (for both electrons and holes) at the interface. For the DCM doped AlQ_3 system, the transport of electron in the host AlQ_3 can be strongly influenced by the DCM molecule which has a higher reduction potential than the AlQ_3 host. DCM, therefore, can act as an electron trap in the AlQ_3 host matrix, affecting the charge transport and consequently the electron-hole recombination processes which result in electroluminescence.

Proposed Mechanism for EL. Two mechanisms can be envisioned as shown in Scheme 1. The *exciton model* assumes the electron-hole recombination in the host near the vicinity of the interface between the hole-transport layer and the emitter, resulting in exciton generation in the host AlQ_3 matrix. Subsequently, these excitons diffuse and then get trapped by the dopant, resulting in emission primarily from the latter. This model is perhaps more appropriate for the EL system such as coumarin 6/AlQ_3 where *coumarin 6* does not appear to act as an electron trap in the AlQ_3 host (6). The lower reduction potential for *coumarin 6* (-1.46 v *vs* -1.79 v for AlQ_3) also suggests that it is less effective as an electron trap in comparison with the DCM class of molecules (*ca.* -1.27 v). A consequence of this model is that the concentration dependence of EL should be more closely resemble that of the PL. This indeed is the case for coumarin 6/AlQ_3 system (1).
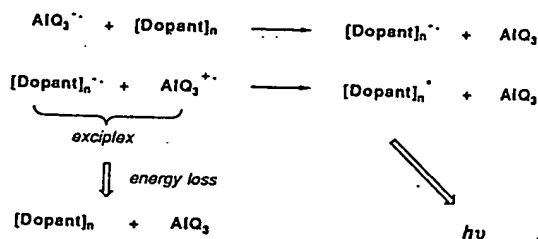
In order to explain the concentration dependence of the DCM/AlQ_3 system, it is necessary to involve a different model involving *charge carrier trapping* by the DCM in the AlQ_3 matrix. Here, DCM in either monomer or aggregated form acts as an electron trap, impeding the transport of the carrier from the cathode to the hole transport interface. Once the negative carrier is trapped in the DCM, the hole has to be drawn into the bulk of the host matrix, presumably via the transport of holes in AlQ_3. The recombination of the trapped electron and the hole in AlQ_3 may result in additional nonradiative pathway such as

the one involving the exciplex between DCM and AlQ$_3$. Furthermore, the trapping of electron by the DCM molecules located near the cathode would result in electron-hole recombination at its proximity, resulting in additional radiative quenching by the cathode.

Exciton Migration Model (Coumarin-6):

$$AlQ_3^{-\cdot} + Ar_3N^{+\cdot} \longrightarrow AlQ_3^{\cdot}$$

$$AlQ_3^{\cdot} + [Dopant]_n \longrightarrow [Dopant]_n^{\cdot} + AlQ_3$$

$$[Dopant]_n^{\cdot} \longrightarrow [Dopant]_n + h\upsilon$$

Electron Trapping Model (DCM and DCJs):

$$AlQ_3^{-\cdot} + [Dopant]_n \longrightarrow [Dopant]_n^{-\cdot} + AlQ_3$$

$$[Dopant]_n^{-\cdot} + AlQ_3^{+\cdot} \longrightarrow [Dopant]_n^{\cdot} + AlQ_3$$

$$\underbrace{\qquad\qquad\qquad}_{exciplex}$$

$$\Downarrow energy\ loss$$

$$[Dopant]_n + AlQ_3 \qquad\qquad h\upsilon$$

Scheme 1. Proposed Mechanism of Electroluminescence.

4. CONCLUSION

In this study, we found that the performance of the *red* organic EL emitter can be optimized by selecting the proper dopants (DCJ vs DCM) and by designing and synthesizing dopant molecules with *steric* bulkiness (DCJT vs DCJ). The steric spacer is important in reducing the effect of concentration quenching inherent in this class of molecules with strong dipoles. The discrepancy between the PL and EL dependence on dopant concentration suggests that electron trapping by the more easily reduced dopant plays an important role in electroluminescence.

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